Platinum Metals as Components of Catalyst-Membrane Systems

By Professor V. M. Gryaznov
A. V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Moscow

Platinum group metals are extensively used as catalysts both in dispersed form and as solids. During recent years we have been witnessing the rapid and successful development of a new branch of catalysis, namely the creation of catalyst-membrane systems. The system combines a catalyst and a membrane which has selective permeability for one of the reagents. Platinum group metal catalysts ensure higher target product yields and durability than other catalysts.

In general, catalyst-membrane systems enhance both reaction rate and selectivity, due to directed transfer of energy and reagents (1). Three functional variations of catalyst-membrane systems have been investigated:

(a) One of the initial reactants, for example hydrogen, reaches the catalyst through the membrane, which is permeable for this substance only. The second reactant comes from a gaseous or liquid phase.

(b) One of the reaction products is selectively removed through the membrane.

(c) The substance penetrating through the membrane is being formed on the catalyst adjacent to one surface of the membrane, this then diffuses through the membrane and reacts at its other surface on the second catalyst with the substance being introduced from the gaseous or liquid phase.

In the first case the catalyst-membrane system provides independent control of the surface concentrations of the two reagents in order to suppress their competing adsorption which is harmful, but inevitable on conventional catalysts. For example during phenol hydrogenation on palladium-ruthenium alloy foil, the cyclohexanone yield decreases very rapidly with time if hydrogen is fed in as a mixture with phenol vapour, see Figure 1(a). However, if hydrogen penetrates through the foil to the surface which is in contact with

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**Fig. 1** The time dependence of the cyclohexanone yield during phenol hydrogenation on a palladium-ruthenium alloy foil, supplied with: (a) hydrogen in a mixture with phenol vapour and (b) with hydrogen passing through the membrane catalyst.
Fig. 2 Cyclohexane conversion is shown as a function of the flow rate of: (a) argon and (b) a mixture of argon with 1,3-pentadiene vapour along the other surface of the palladium-ruthenium foil. The mole fractions of cyclohexane and 1,3-pentadiene in the initial mixtures with argon are equal to 0.17 and 0.12, respectively.

phenol vapour, the product yield is much higher, see Figure 1(b). In this case the foil is acting as both the catalyst and the membrane. Under optimal conditions 92 per cent of phenol is hydrogenated on the catalyst in one step into cyclohexanone, which is used for the production of nylon-6.

In the second case the reaction rate increases due to the removal from the reaction zone of the obtained product as it passes through the membrane. Thus the reaction rate of cyclohexane dehydrogenation increases with the removal through the palladium-ruthenium foil of the hydrogen formed. The catalyst in this reaction contains 0.4 per cent platinum and 0.4 per cent rhenium supported on alumina. The catalyst pellets are represented by circles in Figure 2. On increasing the velocity of the inert gas flow, \( V_A \), which washes the other surface of the membrane, cyclohexane conversion rises dramatically, Figure 2(a) lower curve, and attains the equilibrium degree of conversion, indicated by the blue line, which is obtained under the same conditions but without hydrogen withdrawal. It also works for much lower \( V_A \) values when the cyclohexane feed rate is four times smaller, and its conversion reaches 0.93, as indicated by the upper curve of Figure 2(a). If, however, the palladium-ruthenium foil is replaced by a steel plate (non-permeable to hydrogen) which is covered by a palladium-ruthenium alloy layer, then cyclohexane conversion is reduced to the values shown by the points on the ordinate axis of Figure 2(a).

The two catalysts shown in Figure 2 permit the use of hydrogen, which is removed through the palladium-ruthenium foil, for the hydrogenation of 1,3-pentadiene (see right hand scheme). Thus reaction coupling takes place on the catalyst-membrane system. This illustrates the third type of catalyst-membrane system.

As compared with hydrogen removal by the inert gas, the degree of cyclohexane dehydrogenation increases when reactions are so coupled; which can be seen in Figure 2(b), where the curves lie higher than the respective curves of Figure 2(a). The dotted curve shows pentadiene conversion into the products of selective hydrogenation, which are pentenes, the selectivity of which attains a maximum of 98 per cent. Under these conditions the conversions for both cyclohexane and pentadiene reach 0.99. Experimental evidence of such reaction coupling was found independently in the U.S.S.R. (2) and in the U.S.A. (3), some 25 years ago. Later, coupled reactions were studied on hydrogen permeable palladium alloys in the form of foils and thin-walled...
tubes (4–7). A system analogous to that shown in Figure 2 was used for coupling butane dehydrogenation and hydrogen oxidation (6). The system consisted of a commercial aluminochrome oxide catalyst and a palladium-ruthenium alloy foil. The foil served both as the hydrogen permeable membrane and as the catalyst for the oxidation of hydrogen by air, which was fed along the other surface of the foil. A similar system, comprising an alumino-platinum catalyst and a palladium tube, has been used for cyclohexane dehydrogenation (8, 9).

Types of Catalyst-Membrane Systems

Monolithic Membrane Catalysts

Some materials are both catalytically active and selectively permeable. Palladium and its alloys have been extensively studied for hydrogen evolution or consumption (10–12), and silver has been used for partial oxidation. A non-porous membrane catalyst made of these materials may be called monolithic. Foils and tubes made of palladium alloys are monolithic catalysts permeable only for hydrogen. Such monolithic membrane catalysts with smooth surfaces are easily produced by foil rolling and seamless tube drawing and are commercially available in Russia. Palladium foil alloys can vary from 100 to 10 μm in thickness; tube has a wall thickness of 50 μm and an outer diameter of 0.6 mm. The foils are active both for hydrogenation and dehydrogenation reactions and also possess higher hydrogen permeability than pure palladium and some other industrially used alloys. A thin walled palladium alloy tube twisted into the form of a spiral is shown in Figure 3. This tube can be used as a liquid phase hydrogenation catalyst. Hydrogen is fed into it when the tube is submerged into the liquid to be hydrogenated and heated to the required temperature. The effect of the structures of the substituted allyl alcohol and propargyl alcohol on the hydrogenation rate (13) and on the kinetics of the hydrogenation of phenylacetylene to styrene have been studied on such catalyst systems (14). The latter reaction is of interest because phenylacetylene admixture in styrene complicates the polymerisation. With hydrogen diffusing through the membrane catalyst the phenylacetylene hydrogenation rate is ten times higher than in experiments where hydrogen is bubbled into the hydrogenated substance, and selectivity to styrene reaches 0.92.

Methods for the hermetic connection of foil sheets or tube bundles to other parts of the reactor system have been described (11).

The reactors, one of which is also shown in Figure 3, have successfully withstood pilot-plant tests at temperatures up to 973 K and pressure drops up to 10 MPa. These reactors
can also be used for hydrogen extraction from reforming gases, the product gases of methane steam conversion and also the purge gases of ammonia synthesis.

The merits of monolithic membrane catalysts are: durability and reliability, stability at high temperatures and during thermocycling in hydrogen; resistance to corrosion and mechanical damage, so practically excluding precious metal losses; and the reaction products are readily separated, this being especially important for creating flexible and ecologically pure technologies.

A monolithic membrane catalyst, permeable only for hydrogen, is shown in Figure 4(a), which represents a cross-section through palladium alloy foil sheet or tube wall.

The drawback of monolithic catalysts is the low ratio of their surface area to noble metals volume, which can be increased by roughening one or both surfaces of the membrane catalyst, for example by thermal diffusion of a chemically active metal into the palladium alloy sheet and the subsequent removal of this metal by an acid treatment. The porous layers, Figure 4(b), formed in this way are strongly bound to the palladium alloy sheet and are not dispersed during the reaction, unlike Raney catalysts. A certain part of the chemically active metal introduced into the palladium alloy remains after the acid treatment. Thus the membrane catalyst can be modified in a different way on both surfaces if a reaction coupling is to be performed.

A monolithic membrane catalyst can also be modified by introducing ultra-dispersed particles of catalytically active metal or oxide into these porous layers, as is depicted schematically in Figure 4(c).

**Porous Membrane Catalysts**

Porous membrane catalysts are characterised by higher, but less selective, gas permeability than monolithic catalysts. Sheets obtained from metal powder can serve as the matrix for such porous membrane catalysts. Some porous metals, such as activated porous nickel, are catalysts for hydrocarbon reactions. A porous membrane with catalyst particles distributed throughout its volume is...
presented in Figure 4(d). An example of such a system is a catalyst prepared by inserting into a porous stainless steel sheet 1.5 weight per cent of palladium in the form of ultra-dispersed powder, produced by the condensation of metal and toluene vapours, followed by melting of the resultant glassy solid. This catalyst gives a 25 times larger yield of linalool than the same weight of palladium used in the form of a palladium-6 per cent ruthenium foil, 50 μm thick, through which hydrogen diffuses during dehydrolina-lool hydrogenation into linalool, at a temperature of 443 K and at atmospheric pressure. The monolithic membrane catalyst has higher selectivity (0.99) than the porous catalyst (0.90), although a selectivity of 0.95 can be achieved on the porous membrane catalyst by a decrease in space velocity.

The porous metallic membrane catalyst differs from the conventional supported metal catalyst by having a higher mechanical stability and better heat conductivity than most supports used for industrial catalysts. The porous metallic membrane also provides certain selectivity for mass transfer.

To save catalytically active metal its particles need only be introduced into the sub-surface layer of the porous membrane which may be metallic, oxide, ceramic or polymeric form, see Figure 4(e).

The advantages of porous and monolithic membrane catalysts can be happily combined in composite membrane catalysts.

Composite Membrane Catalysts

Composites comprising a mechanically stable porous support and a thin but continuous palladium alloy layer enable expenditure on platinum group metals to be decreased and hydrogen permeability to be increased. Such composites can be readily obtained, for example by diffusion welding a palladium alloy foil, 10 μm thick, to a porous metal sheet. An intermediate layer, Figure 4(f), is used to prevent the transfer of components between the support and the alloy, and also to augment adhesion.

A palladium film 20 μm thick, deposited by chemical reduction of a palladium salt onto the outer surface of the porous glass cylinder, with an average pore diameter of 300 nm (15), has been used at 673 K to remove hydrogen from the products of the water gas shift reaction over an iron-chromium oxide catalyst (16, 17) and for steam conversion of methane on an industrial nickel catalyst (18, 19).

A non-porous palladium layer of about 5μm thick has been obtained by chemical plating onto a silver disc, with a pore diameter of 0.2 μm (20). This composite membrane was tested for hydrogen permeability at temperatures up to 680 K and appeared to be resistant to pressure drop as well as being stable to thermocycling in hydrogen.

Composite membrane catalysts can also be assembled with polymeric supports or intermediate layers (21–23). The use of polyaryldie has been proposed by investigators at this Institute, in order to widen the temperature range of their application (24). Polyaryldie is resistant in air up to 623 K, and its hydrogen from nitrogen separation factor is about 100.

Asymmetric membranes have been created at the A. V. Topchiev Institute of Petrochemical Synthesis and at the Chemical Machine Building Institute. When such polyaryldie membranes are covered with a 1 μm palladium alloy layer they possess higher permeability for hydrogen than non-metallised membranes at temperatures greater than 373 K, and are not permeable for other gases.

At even higher temperatures composite membranes of porous metals, oxides, ceramics and thin palladium or palladium alloy layers are used. At the Patrice Lumumba Peoples' Friendship University a method of obtaining thin alloy films containing a low melting component has been developed (25). This component, being liquid, coats the porous membrane, and after it has hardened other components are introduced by magnetron sputtering. The whole system is then annealed to make it homogeneous. A composite palladium-indium-ruthenium alloy layer was prepared by liquid indium distribution over a
porous stainless steel sheet, or over a magnesia plate, with subsequent palladium-ruthenium alloy magnetron sputtering. This 2 \mu m thick three-component alloy layer only allows hydrogen to permeate, at a speed of 10 m^3/m^2 per hour at 673 K and at a pressure drop of 0.2 MPa. Such a composite has retained all the above mentioned characteristics after 450 cycles of heating and cooling in hydrogen.

A system comprising a porous support, an intermediate layer and a film made of a selectively permeable and catalytically active material, may be covered by a polymer, see Figure 4(g), which allows the feedstock to permeate but which keeps out catalyst poisons. A porous metallic sheet covered by a polysiloxane layer was used to fix silica gel particles, on the surface of which palladium complexes were immobilised (26). Such a system proved to be active for the selective hydrogenation of cyclopentadiene into cyclopentene.

A composite catalysts for reaction coupling should comprise five layers, as shown in Figure 4(h), consisting of a porous membrane with intermediate layers and films of catalysts I and II on its surfaces.

Granulated and Membrane Catalysts Systems

Of even more general purpose are the systems containing a conventional granulated catalyst and a membrane catalyst. Figure 4 shows two varieties of such a system: a pellet catalyst with a monolithic catalyst, 4(i), and with a composite membrane catalyst, 4(j).

A system, consisting of an industrial oxide aluminochromium catalyst and a hydrogen permeable palladium alloy foil containing 20 weight per cent of silver, has been used for butane dehydrogenation (27). Part of the hydrogen formed was removed through the membrane, with inert gas being fed along the other membrane surface at 673 K and atmospheric pressure, and this resulted in butene yields of 18 to 25 per cent and butadiene yields of 0.8 to 1.4 per cent.

The influence of butane and its dehydrogenation products on the hydrogen permeability of a series of binary palladium alloys has been investigated (6). Butane conversion increased when an air flow was used instead of an inert gas flow to remove the hydrogen which had penetrated through the membrane. A similar result was obtained for butene-1 dehydrogenation on an aluminochromium oxide catalyst (28), with hydrogen withdrawn through a 25 \mu m thick palladium foil, on the other side of which an argon mixture containing 10 per cent oxygen was fed. For example, at 658 K and a butene feed rate of 5 ml/min, oxidation of the hydrogen which had diffused through the membrane increased the butene conversion rate by a factor of three, compared with equilibrium conditions without hydrogen withdrawal (29).

Systems containing a pellet catalyst and a hydrogen permeable composite membrane, Figure 4(i), have been used to intensify propane aromatisation (30) and steam conversion of methane (19). ZSM-5 zeolite, with gallium ions introduced by ion exchange, catalysed propane aromatisation. The zeolite was arranged in the central part of a cylindrical reactor, which had a coaxial porous alumina tube, the outer surface being coated with a palladium film 8.6 \mu m thick. An equimolar propane-nitrogen mixture was fed into the space between the tubes, while the inner tube volume was pumped. To elucidate the function of the membrane, the coated alumina tube was replaced by a non-permeable pyrex tube. The yield of aromatic hydrocarbons was 42 per cent with the pyrex tube, and rose to 76 per cent when about 90 per cent of the hydrogen formed was removed. This phenomenon was explained by hydrocracking and by enhancing propane dehydrogenation into propene, out of which a considerable amount of naphthalene was formed, when a gallium-containing ZSM-5 catalyst was used (31).

Steam conversion of methane was studied in a similar reactor over a nickel catalyst, with a tubular porous glass membrane (average pore diameter 300 nm) coated with a 20 \mu m thick
palladium layer. Methane conversion reached 78 per cent at 773 K when the hydrogen diffusing through the membrane was removed by a flow of nitrogen, while equilibrium methane conversion without hydrogen withdrawal amounted to 44 per cent.

This classification of catalyst-membrane systems summarises and generalises the versions suggested earlier (32, 33).

**Catalytic Membrane Reactors**

Membrane reactors are subdivided into ten types according to the following criteria: catalyst application in reaction side and in separation side; membrane functioning only for separation or also as a catalyst; removal of the gas passing through the membrane as it is or by the introduction of a gas into the reaction (9).

A mathematical simulation of a catalytic membrane reactor and an inert membrane reactor with catalyst pellets in the feed side showed a slight advantage of the former at not too small space velocities (34) which is in good agreement with experimental data for cyclohexane dehydrogenation into benzene. A porous glass thimble, with 0.34 weight per cent platinum introduced into its pores, served as the membrane catalyst. In this case the reaction took place in the membrane catalyst itself, see Figures 4(d) or 4(e). The membrane made of the same porous glass without any metallisation was catalytically inert, and had to be used with a layer of platinised porous glass particles on it.

A porous membrane catalyst of the type shown in Figure 4(e) was obtained by introducing 1 weight per cent platinum into the pores of a multi-layered tubular alumina membrane (Membralox®, Alcoa). It provided a six-times greater yield of ethylene from ethane dehydrogenation than equilibrium without hydrogen withdrawal (35). Selectivity towards ethylene was more than 0.96. Ethane transfer through the porous membrane catalyst occurred at a rate four-times slower than hydrogen transfer. A mathematical model of the reactor with this catalyst has been worked out, and it represents, very satisfactorily, the experimental results when parameter adjustments have been made.

Mathematical models of a catalytic membrane reactor, an inert membrane reactor with catalyst pellets, a plug flow reactor packed with catalyst pellets, and also a mixed flow reactor have been created (36). It was found that for liquid phase reactions without any volume changes, the first two types of reactors are preferable at high space velocities. It is also true for an inert membrane reactor with catalyst pellets for reactions with a volume decrease, but it does not work as well as a catalytic membrane reactor at a low pressure drop on the membrane.

Investigations using a catalytic membrane reactor with a palladium membrane showed that when the dehydrogenated substance and the hydrogen carrier gas, coming through the membrane, flow in opposite directions the degree of conversion is the highest at a minimal reactor length, if compared with the regimes of co-current, ideal mixing in the reaction chamber, hydrogen collection chamber or in both of them (37). While these mathematical models were being created it was assumed that hydrogen transfer through a palladium membrane is described by the Sieverts law. It was proved experimentally, however, that in the process of butane dehydrogenation on palladium alloy foils the hydrogen permeability decreases, not because of the butane but as a result of the adsorption of butenes (6, 38). This effect is even more pronounced for palladium-antimony alloy than for ruthenium-palladium alloy. When the membrane ceased to be hydrogen permeable, due to strong adsorption of butenes, these butenes are then not subject to isomerisation or to hydrogenation in the hydrogen flow from the gaseous phase. If, however, hydrogen transfer through the membrane is only decreased by butene adsorption then only isomerisation of butenes occurs, and not hydrogenation. These results led to the assumption that in butene isomerisation and hydrogenation reactions hydrogen atoms entering the active centres of
the membrane catalyst from its sub-surface layer are of great importance.

A study of the influence of electron acceptors (S, CO) and electron donor (K) adsorption on the hydrogen permeability of palladium-silver alloy concluded that the species passing through the alloy is not H⁺ (39). Hydrogen permeability decreased after contact with the ethylene, but in the process of ethylene hydrogenation by hydrogen, passing through the same foil, a 10-fold increase in permeability was observed.

Another study has been performed to investigate the effect of the directions of flow of the hydrogenated substance and of the hydrogen along adverse surfaces of the membrane catalyst on the hydrogen permeability and also on the depth of cyclopentadiene hydrogenation occurring on a palladium alloy containing 4 weight per cent indium (40). The hydrogen transfer rate to the hydrogenation chamber was higher with a counter flow of hydrogen-nitrogen mixture and cyclopentadiene vapour-nitrogen mixture than with co-current flow. Figure 5 shows the dependence of the degree of cyclopentadiene (CPD) conversion on \( \frac{V_{H_2}}{V_{CPD}} \) feed velocity ratio, for counter-current (Curve 1) and co-current (Curve 2) flows. The amount of hydrogen transferred through the membrane catalyst during different flow directions was kept constant by changes in the composition of the hydrogen-nitrogen mixture.

During the coupling reactions of terpene alcohol: borneol dehydrogenation into camphor, on a copper catalyst, with cyclopentadiene hydrogenation on palladium-ruthenium alloy foil, counter-current flow again proved to be more effective than co-current flow (41). As Figure 6 depicts, the cyclopentene concentration (Curve 1) in the cyclopentadiene hydrogenation products is much higher for counter-current flow and decreases more slowly during the course of the experiment than for co-current flow, see Figure 6(b). The camphor yield from borneol was 93 per cent. In the counter-current coupling of cyclohexane dehydrogenation and 1,3-pentadiene hydrogenation, discussed earlier and shown schematically in Figure 2, a 20 per cent increase in selectivity for pentenes was obtained, compared with using co-current conditions (42).

Structurally, a catalytic membrane reactor can resemble a block made up of corrugated

![Fig. 5 The conversion of cyclopentadiene is dependent on the ratio of hydrogen: cyclopentadiene in the feed velocities for both counter-current (Curve 1) and co-current (Curve 2) flows](image)

![Fig. 6 Time dependence of the concentrations of cyclopentene (Curve 1) and cyclopentane (Curve 2) as products of cyclopentadiene hydrogenation by hydrogen coming through the palladium-ruthenium during borneol dehydrogenation on the other surface of the foil: (a) counter-current and (b) co-current flows](image)
and plane sheets obtained by roasting mixtures of inorganic oxide powders, binders and plasticisers. Having parallel orientation, each pair of corrugated sheets is separated by a plane sheet and thus parallel channels are formed. Every second corrugated sheet is turned through 90° with respect to the first, thus two similar channel systems will be perpendicular to each other (43). Such blocks can be manufactured out of porous metal sheets, as mentioned earlier. Blocks with perpendicular channel systems are convenient for separating the flows along both sides of the membrane catalyst.

The catalyst material may also be deposited on alumina multi-channel membrane elements to produce catalytic membrane reactors (44). Methods of depositing platinum group metals on solid supports of different composition, as well as on porous ones, have been investigated at the Patrice Lumumba Peoples’ Friendship University and at the A. V. Topchiev Institute of Petrochemical Synthesis of the Russian Academy of Sciences.

The palladium based monolithic membrane catalysts proposed by the above named institutions, in collaboration with A. A. Baikov Institute of Metallurgy of the Russian Academy of Sciences, could be successfully combined with conventional catalysts for the dehydrogenation or steam conversion of hydrocarbons. The apparatus for extracting pure hydrogen by diffusion (45), and hydrogen generators incorporating catalytic cracking and silver-palladium diffusion units (46), could also be equipped with the above mentioned palladium alloy membranes thus giving high hydrogen permeability for the products of hydrocarbon transformations.

Five years ago membrane reactor catalysts, along with two other types of catalyst, were said to have high potential to make a major impact on new catalyst technology for the future (47). Clearly the new data about catalyst-membrane systems fully justifies those expectations.

**Conclusions**

Combining catalysts and membranes has become a most promising method for improving existing technologies. It seems likely that the suggested classification of catalyst-membrane systems will be helpful in further investigations.

Several types of catalytic membrane reactor have now been studied both theoretically and experimentally. The results have proved to be very encouraging, especially for thermodynamically complicated reactions. Palladium alloys which maintain their hydrogen permeability when in contact with dehydrogenation products have been found. Such membranes are good for use in combination with hydrocarbons dehydrogenation catalysts and can be used as catalysts for the oxidation of the removed hydrogen, thus compensating for the endothermicity of dehydrogenation.

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*Platinum Metals Rev.*, 1992, 36, (2) 78
Platinum-Iridium Carbon Monoxide Sensor

Various heat of oxidation and doped metal oxides types of catalytic sensors have been used in gas detectors, but in general they suffer from interference caused by water vapour. These changes in humidity can produce spurious signals which have in the past been overcome by the use of high power heaters.

In order to solve the humidity-effect problem that occurs with catalytic carbon monoxide sensors and to eliminate the requirement for heaters, researchers at the Chalk River Laboratories of AECL Research, in cooperation with Asahi Electronics Inc., Ontario, Canada, have developed and tested several new bimetallic platinum group metal catalysts, (K. Marcinkowska, M. P. McGauley and E. A. Symons, Sens. Actuators B, 1991, 5, (1–4), 91–96). The optimised catalyst contained a total of 10 weight per cent of platinum and iridium which was supported on porous, inertly hydrophobic polystyrene-divinylbenzene granules contained in nylon mesh thimbles.

This new carbon monoxide sensor was found to be independent of humidity and even after testing for 10 months, no affect on the carbon monoxide oxidation activity of the catalyst was detected despite exposure to carbon monoxide concentrations of up to 250 ppm.

The sensor requires no heater as the catalyst is active at ambient temperatures down to around -10°C. This has facilitated production of a portable, battery-powered detector.